Chemistry in Action:
Space Shuttle Fuel Chemistry

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Outline

- **Student's Perception of Chemistry**

- **Role In Science and Technology**
  - **Traditional Areas**
  - **Recent and Emerging Technologies**

- **Space Shuttle-Atmospheric Interactions**

- **New Hypergolic Fuels**

- **Closing Remarks**
  - **Acknowledgements**
  - **Career in the Government**
  - **Web Resources**

Student's Perception of Chemistry

- ❑ **It is too Hard! Too Much Math! I do not Like Cooking!**

- ❑ **It is Only for Academicians!**

- ❑ **What use is it for Getting Good Jobs?**

- ❑ **I Also Thought This! Until I met my Mentor, Ian Worthington**

- ❑ **Definition:**

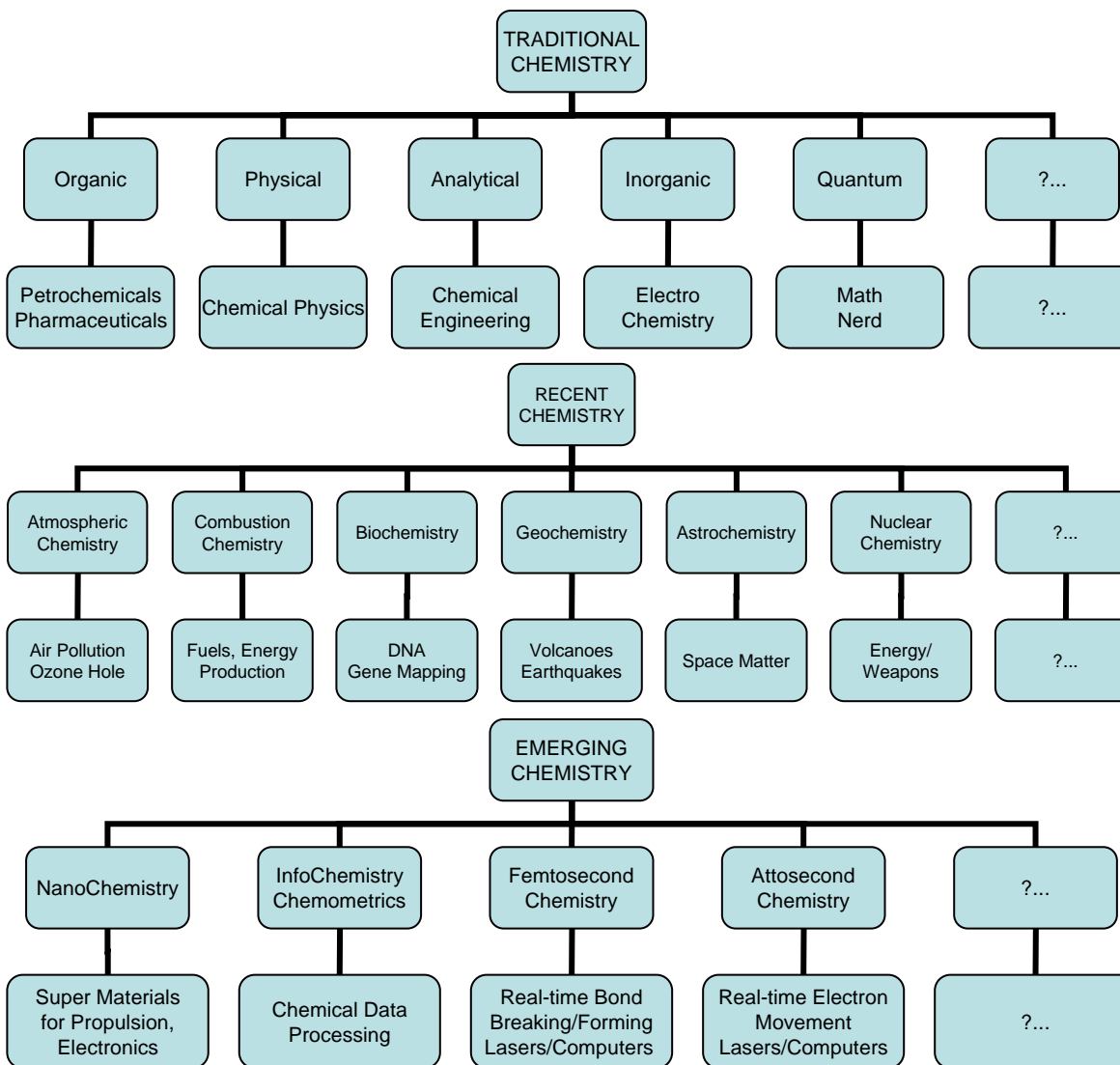 - ❑ **Study of MATTER and the Changes That Take Place With That MATTER**

- ❑ **Importance:**

  - ❑ **MATTER is Everywhere! Therefore it Matters a lot!**

    - ❑ **To Understand the Energetics of Breaking and Making Chemical Bonds**

    - ❑ **We Seek Microscopic Explanation of Macroscopic Changes we Experience**

Role in Science and Technology

TRADITIONAL CHEMISTRY
- Organic → Petrochemicals Pharmaceuticals
- Physical → Chemical Physics
- Analytical → Chemical Engineering
- Inorganic → Electro Chemistry
- Quantum → Math Nerd
- ?... → ?...

RECENT CHEMISTRY
- Atmospheric Chemistry → Air Pollution Ozone Hole
- Combustion Chemistry → Fuels, Energy Production
- Biochemistry → DNA Gene Mapping
- Geochemistry → Volcanoes Earthquakes
- Astrochemistry → Space Matter
- Nuclear Chemistry → Energy/ Weapons
- ?... → ?...

EMERGING CHEMISTRY
- NanoChemistry → Super Materials for Propulsion, Electronics
- InfoChemistry Chemometrics → Chemical Data Processing
- Femtosecond Chemistry → Real-time Bond Breaking/Forming Lasers/Computers
- Attosecond Chemistry → Real-time Electron Movement Lasers/Computers
- ?... → ?...

Space Shuttle Propulsion System

- **Space Propulsion (PRC, OMS, Veneers):**
    - **Hypergolic Liquids**
        - $CH_3NHNH_2 + N_2O_4 \rightarrow$ **products** $+ \Delta H$
            - **NO External Ignition Required!**

- **Boost Phase (2 x 3.1 Mlb):**
    - **Solids**
        - $HTPB + NH_4ClO_4 \rightarrow$ **products** $+ \Delta H$
            - **One-time Squib**

- **Launch (3 x 0.4 Mlb):**
    - **Cryogenic Liquids**
        - $2H_2 + O_2 \rightarrow 2H_2O + \Delta H$
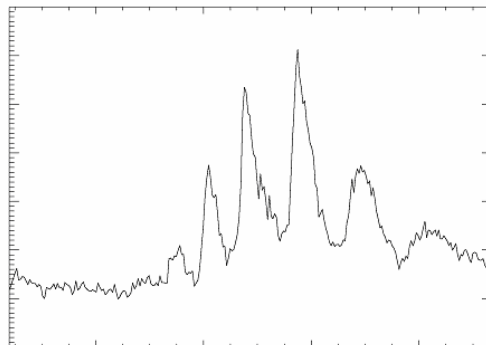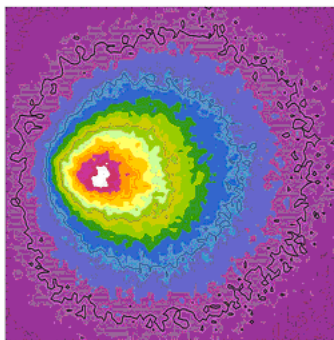   - **One-time Torch**
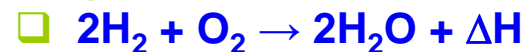
Space Shuttle-Atmospheric Interactions

AFRL's Motivation:

➤ **Understand Chemiluminescent Processes at ≥ 200 Km**
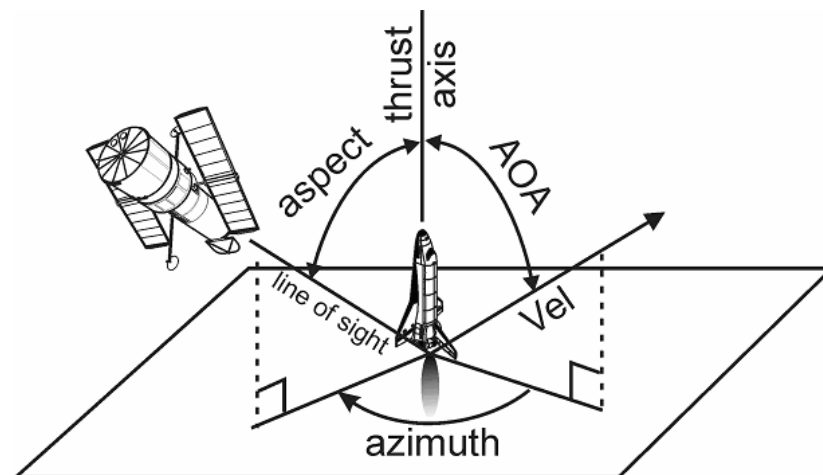
Strong Emissions From CO(a):

Space Experiment

Cause of Chemiluminescence:

Rocket Plume-Atmospheric Interactions

UV-Chemistry Questions:

- **Precursors?**
- **Its Formation?**
- **Its Reactions?**

Observation Platforms

Space Shuttle
Mir Space Station
MSX

Thrusters

Space Shuttle
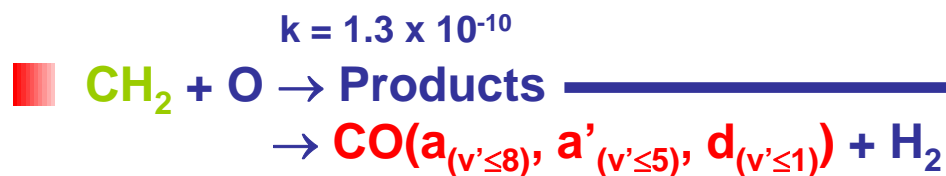Progress-M
Soyuz-TM

Proposed CO(a) Source Chemistry

■ Unreacted $CH_3NHNH_2 \rightarrow \rightarrow$ Precursor(s)
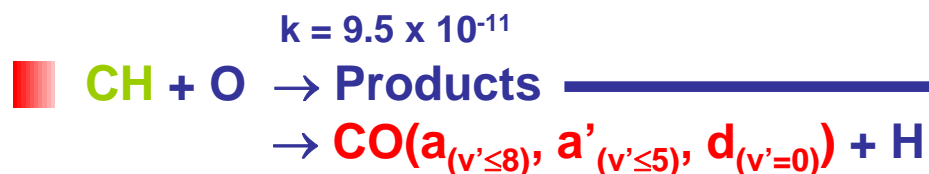
■ Precursor(s) + O $\rightarrow$ Products

> ❏ **200 km-Thermosphere**
> > ❏ $[O] >> [O_2]$

$$\rightarrow CO(a_{(v')}) + R$$

$$\rightarrow CH_2 + OR'$$

$$\rightarrow CH + OR''$$

k = 1.3 x 10⁻¹⁰

■ $CH_2 + O \rightarrow$ Products
$$\rightarrow CO(a_{(v'\leq 8)}, a'_{(v'\leq 5)}, d_{(v'\leq 1)}) + H_2$$

> { $CO + H_2$ (Main)
> $2H + CO$ (~ 20%)
> $H + HCO$ (HCO*)
> $CH + OH$ (~ 6%)

k = 9.5 x 10⁻¹¹

■ $CH + O \rightarrow$ Products
$$\rightarrow CO(a_{(v'\leq 8)}, a'_{(v'\leq 5)}, d_{(v'=0)}) + H$$

> { $CO + H$ (Main)
> HCO (HCO*)
> $HCO^+ + e^-$ (~ 0.03%)
> $C + OH$ (? +ve E_a)

Apparatus

He/CHBr$_3$

He/O$_2$(O-atoms)

vuv-Spectrometer

Calorimeter

248-nm Laser

Pump

uv/vis-Spectrometer

$CHBr_3$ Photolysis
To Produce CH Radicals

$\sigma\ (10^{-20}\ cm^2\ molec^{-1})$

λ (nm)

$CH(^4\Sigma^-) + Br_2$

$Br + HBr + C$ $CH(^2\Pi) + Br_2$ $(Br + Br)$

$CH(^4\Sigma^-) + Br$ $h\nu$

$CH(^2\Pi) + Br$ $h\nu$ $CBr + HBr$ $(H + Br)$

$\uparrow h\nu$ (~25%)   (~75%) $h\nu$

$(\Delta H= -24.8)\ CHBr + Br_2 \leftarrow h\nu + CHBr_3 \rightarrow Br + CHBr_2\ (\Delta H= -49.6)$

$h\nu$ $\downarrow h\nu$ $\downarrow$(?) $h\nu$ $h\nu$

$HBr + C$ $CBr + H$ $CBr_2 + HBr$ $CBr_2 + H$

$h\nu$

$Br + CHBr \rightarrow CH(A) + Br$

$h\nu$ $h\nu$ **431nm**

$CBr + H$ $C + HBr$ CH

$h\nu$

$CH + Br$
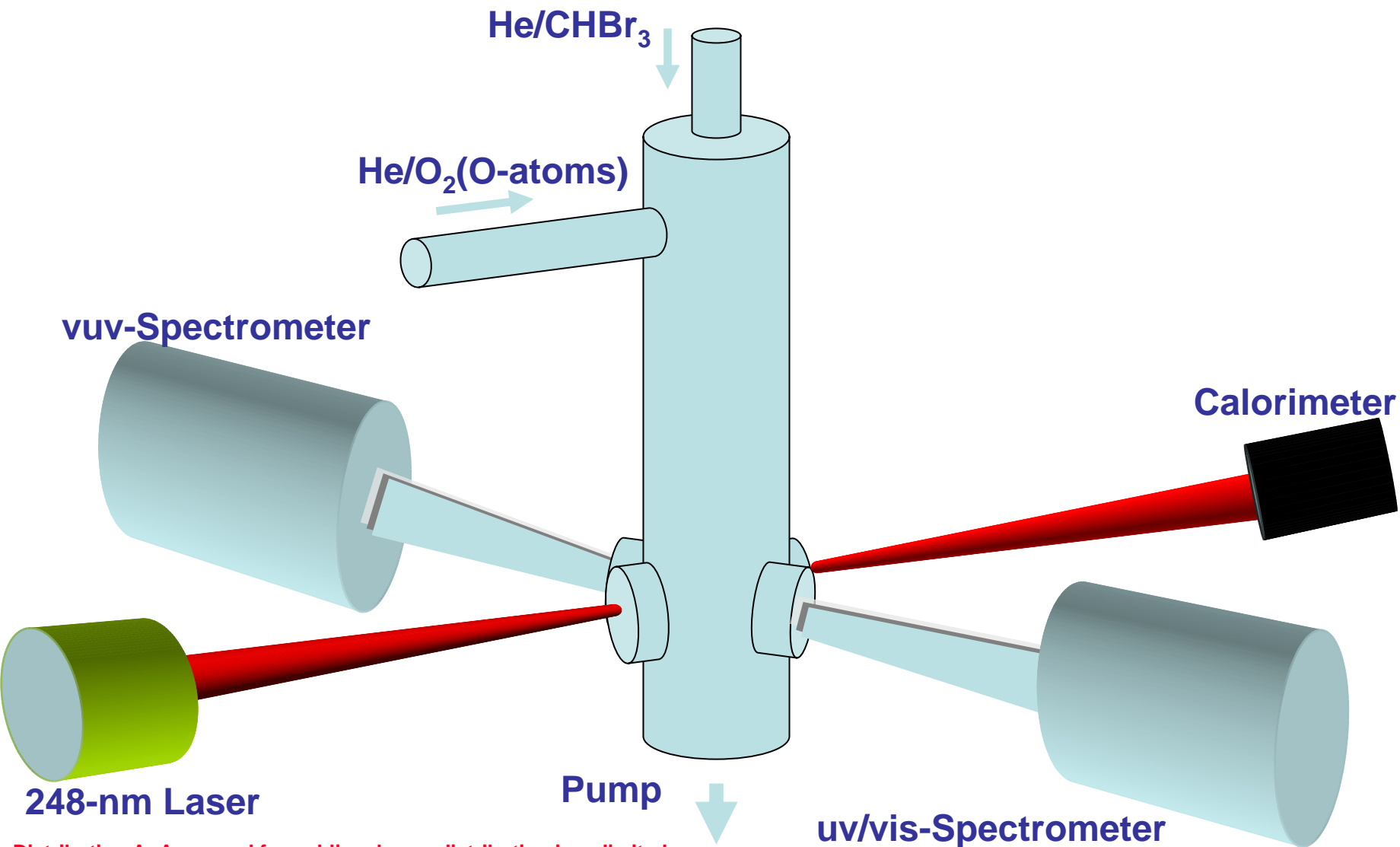
CO(A) Source Reactions

🌸 **Chemiluminescence Intensity Varied as (Laser Fluence)^2**

ΔH^o_{298K}(kcal mol^{-1})

$C(^3P) + O(^3P) \rightarrow CO(A^1\Pi)$ (-71.8)

$CHBr + O(^3P) \rightarrow HBr(X^1\Sigma^+) + CO(A^1\Pi)$ (+1.3)

$CH + O(^3P) \rightarrow H(^2S) + CO(A^1\Pi)$ (+9.2)

$CBr + O(^3P) \rightarrow Br(^2P_{3/2}) + CO(A^1\Pi)$ (+3.8)

$CBr_2 + O(^3P) \rightarrow Br_2(^1\Sigma^+_g) + CO(A^1\Pi)$ (+29.1)
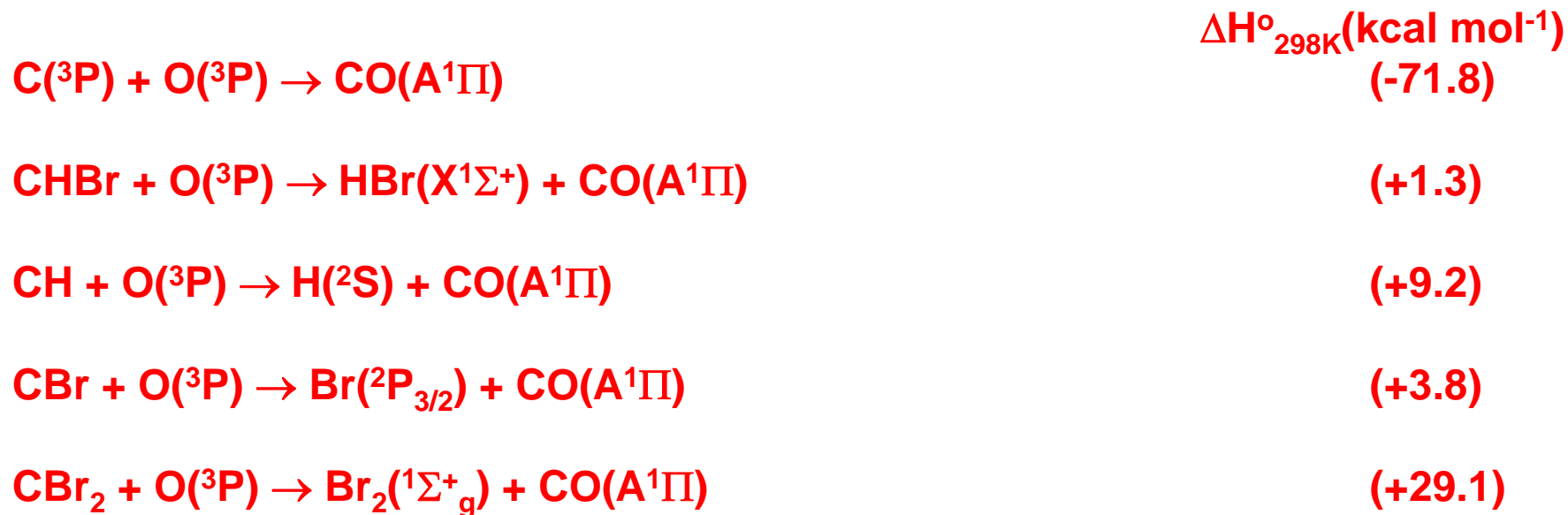
🌸 **Diatomics or Triatomics Need to be Internally Excited**

Comparison of CO & OH-Chemiluminescence

Strong CO(A) Signal in O/O$_2$
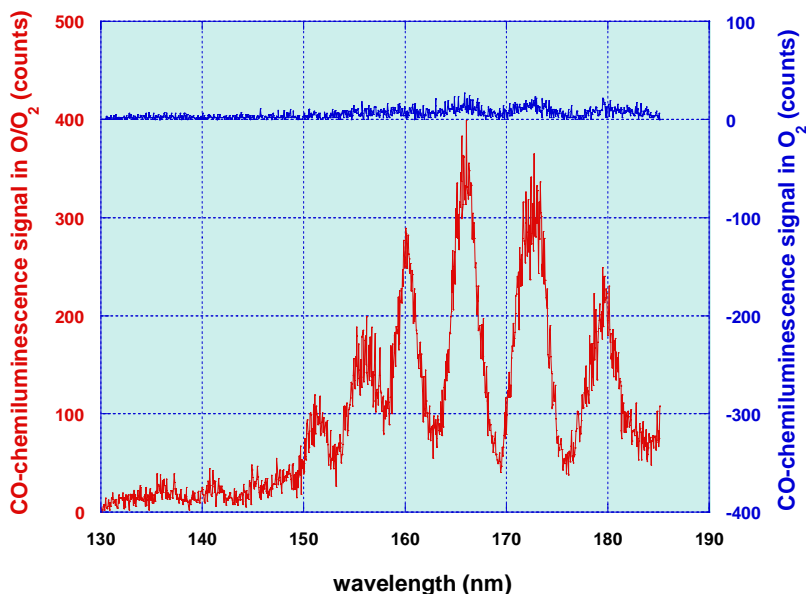
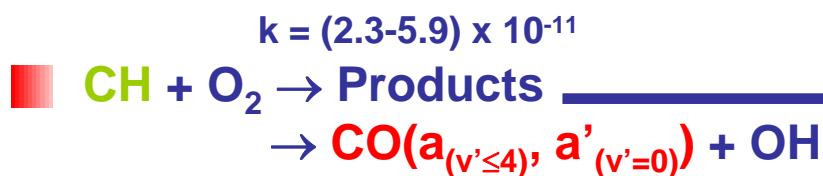**Very Weak CO(A) Signal in O$_2$ only**

Weakened OH(A) Signal in O/O$_2$
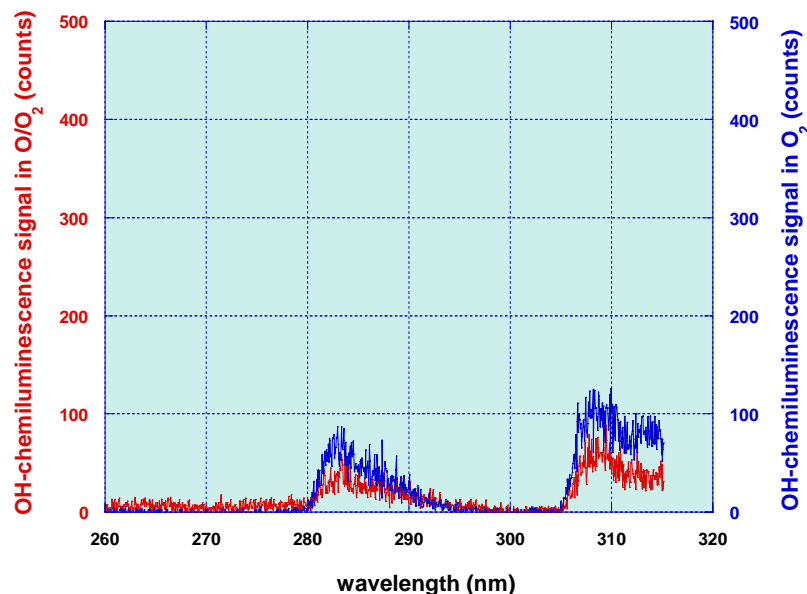
Strong OH(A) Signal in O$_2$ only

$$k = (2.3-5.9) \times 10^{-11}$$

■ **CH + O$_2$ → Products**
  → CO(a$_{(v' \leq 4)}$, a'$_{(v'=0)}$) + OH

{
CO + OH (~ 20%)
CO$_2$ + H (~ 30%)
HCO + O (~ 20%)
H + CO + O (~ 30%)
CO + OH(A) (~ 0.48%)
}

Time-Resolved CO(A)-Chemiluminescence

❑ **Bimolecular Reaction Rate Coefficients of Added Substrate When CH$_4$ Present**

↓

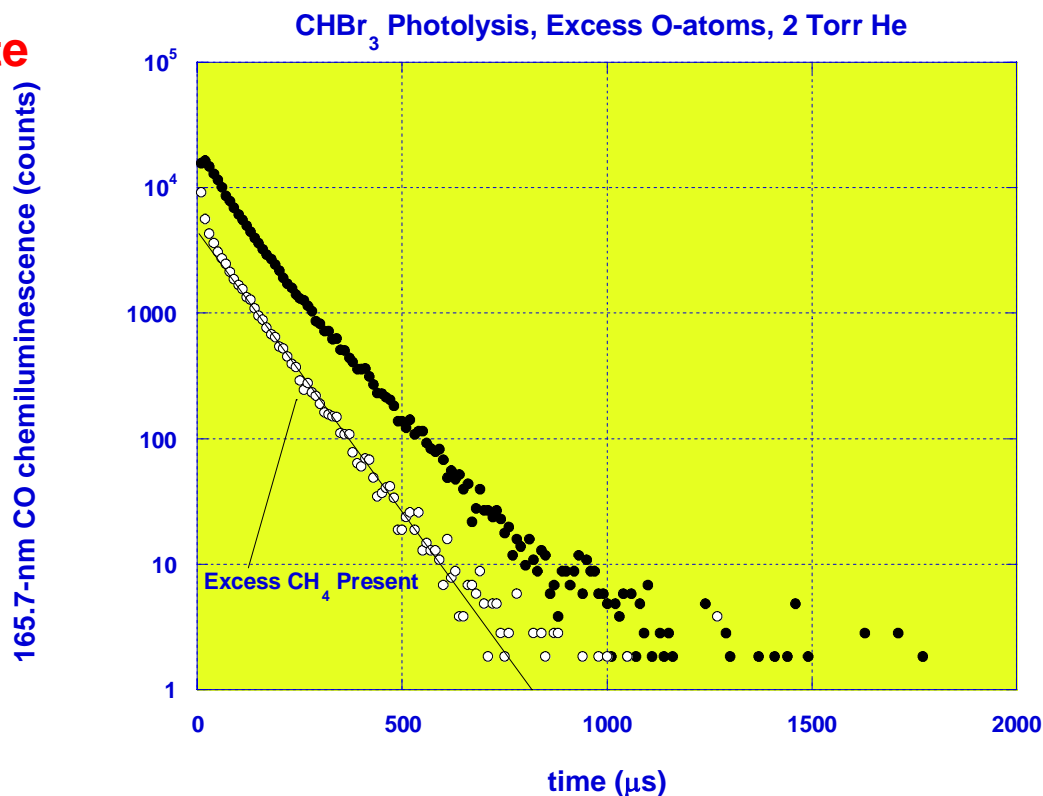$k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$
$k_{N_2O} < 7 \times 10^{-14}$
$k_{NO} = (3.4 \pm 0.5) \times 10^{-11}$
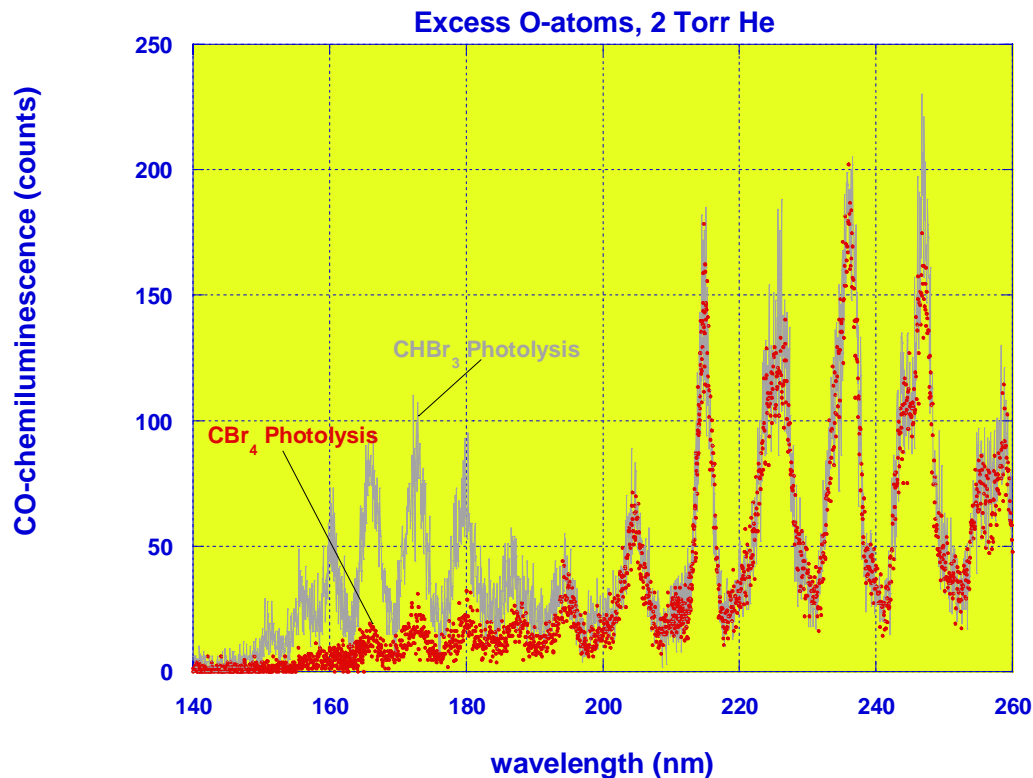$k_{H_2} < 2 \times 10^{-13}$
$k_{CH_4} < 6 \times 10^{-14}$

↓

❑ **(C + O) not the Source**

CHBr$_3$ Photolysis, Excess O-atoms, 2 Torr He

y-axis: 165.7-nm CO chemiluminescence (counts)
x-axis: time (μs)

Excess CH$_4$ Present

CHBr$_3$ Versus CBr$_4$ Photolysis

Excess O-atoms, 2 Torr He

CHBr$_3$ Photolysis

CBr$_4$ Photolysis

- wavelength (nm)
- CO-chemiluminescence (counts)

❑ **Stronger VUV Signal in CHBr$_3$ Photolysis**

↓

(CH# (or CHBr#) + O) Important

❑ **Signal in CBr$_4$ Photolysis Varies as (Fluence)^2**

↓

(CBr$_2$# + O) not Important, Since Br$_2$* Signal Varies as (Fluence)^1

CBr$_4$ Photolysis

Excess O-atoms, 2 Torr He

- chemiluminescence (counts) vs wavelength (nm)
- CO* $\propto$ (Fluence)^2
- Br$_2$* $\propto$ (Fluence)^1
- Laser Off
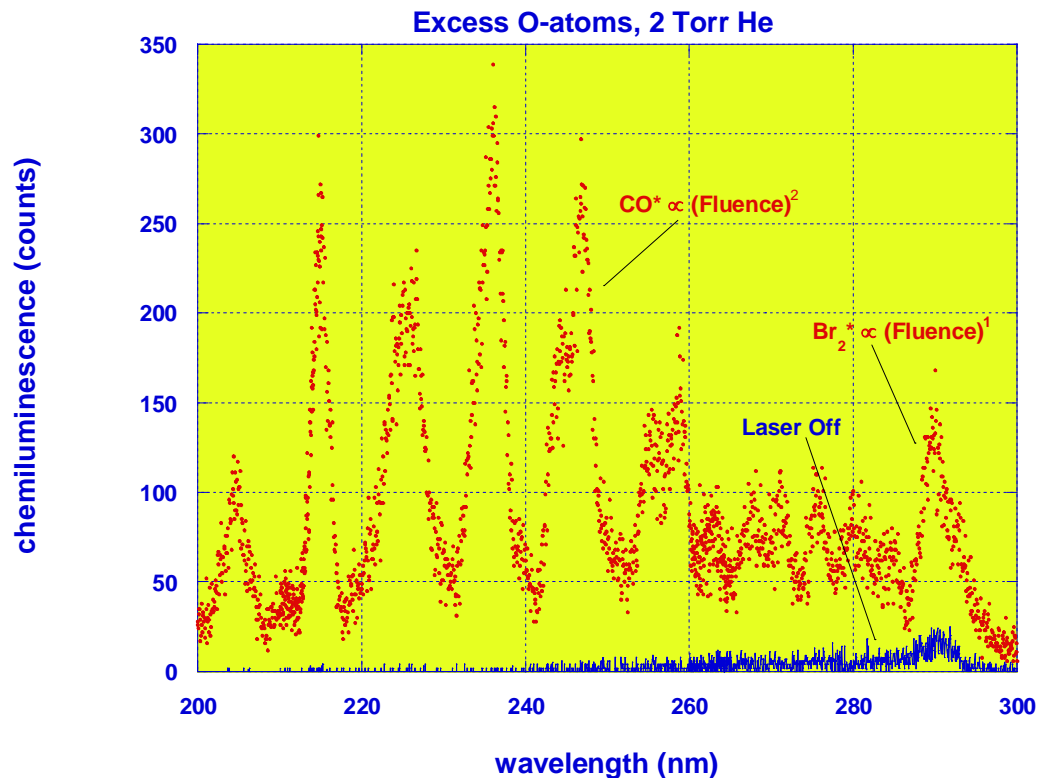
❑ **CBr$_2$ + O $\rightarrow$ CO + Br$_2$***

❑ **CBr$_2$ Formed in Absence of Photolysis**

❑ **CBr$_2$ Formed in Photolysis**

❑ **CBr + O $\rightarrow$ CO* + Br**

$\downarrow$

CBr$_2$ + O $\rightarrow$ CO* + Br$_2$ not Important

CHBr$_3$ Versus CBr$_4$ Photolysis

Excess O-atoms, Excess CH$_4$, 2 Torr He

Plot axes: 165.7-nm chemiluminescence (counts) versus time (μsec). Curves labeled CHBr$_3$ Photolysis and CBr$_4$ Photolysis.
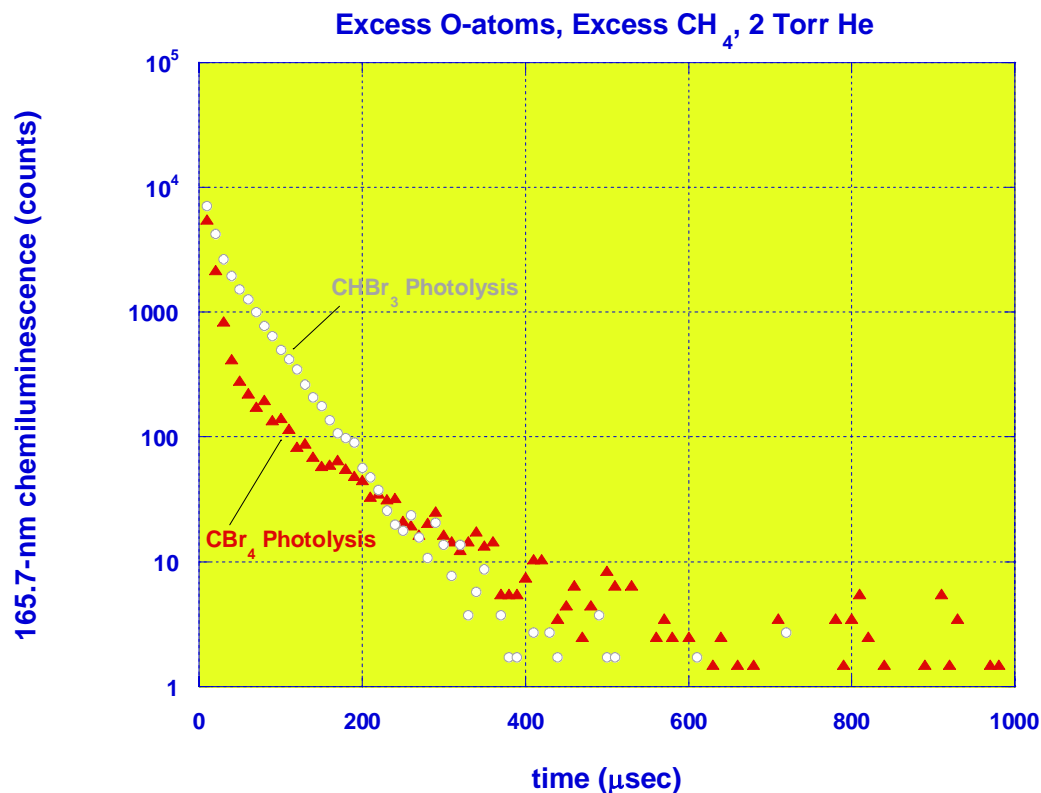
❑ **CHBr$_3$**
$k_{O_2} = (2.2 \pm 0.3) \times 10^{-11}$

❑ **CBr$_4$**
$k_{O_2} = (2.4 \pm 0.4) \times 10^{-12}$

↓

(CBr# + O) Source is not as Important as (CH# + O) in CHBr$_3$ Photolysis

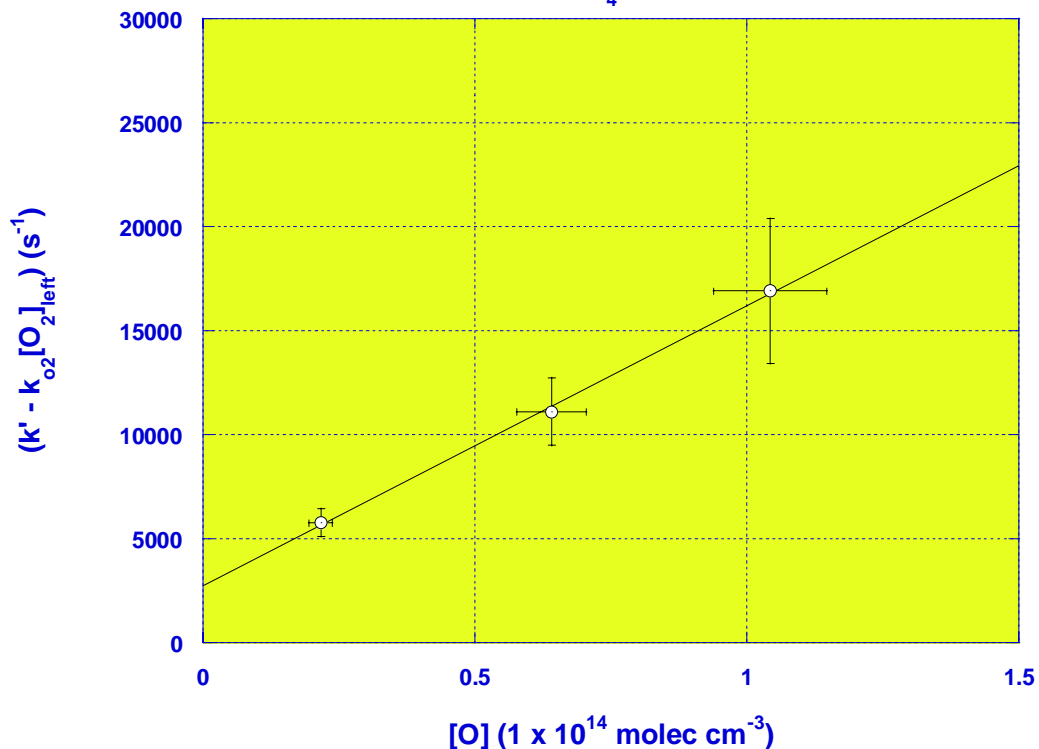❑ **CHBr# has Very Short Lifetime (~ 5 μs) and $k_{(CHBr + O_2)} < 2 \times 10^{-14}$**

↓

(CHBr# + O) Source not Important in CHBr$_3$ Photolysis

CH($a^4\Sigma^-$) + O
Reaction Rate Coefficient

Excess CH$_4$, 2 Torr He

Plot: y-axis **(k' - k$_{o2}$[O$_2$]$_{left}$) (s^{-1})** ranging 0 to 30000; x-axis **[O] (1 x 10^{14} molec cm^{-3})** ranging 0 to 1.5

- $k_{(CH(a) + O)}$ = (1.35 ± 0.47) x 10^{-10}

Previously:
- $k_{(CH(X) + O)}$ = (9.5 ± 1.4) x 10^{-11}

Space Shuttle-Atmospheric Interaction: Conclusions

🟤 **248-nm Photolysis of $CHBr_3$/O-atom Mixtures**

Strong Emissions From:

- 🔵 **CO(A), CO(a)**
- 🔵 **OH(A) when O_2 Present**
- 🔵 **Br_2(D)**

Kinetic & Laser Fluence Trend Analyses of the Chemiluminescence:

- 🔵 **$CH(X^2\Pi, a^4\Sigma^-)$ + O**
- 🔵 **CBr_2 + O**

🟢 **Plume Fragments (CH) + Thermosphere (O-atoms) $\rightarrow$ UV Emissions**

New Hypergolic Fuels

AFRL's Motivation:
- Replace Highly Toxic CH_3NHNH_2 (MMH)
- Design Better Performing Fuels

AFRL's Approach:
- Tune Fuel Structure for;
  - Energy Content: High Heat of Combustion
  - Oxygen Balance: Lower Spacecraft Mass
  - Physical Properties: Higher ρ, Lower mp, Reduced Sensitivities
  - Ignition/Combustion Behavior: Short ID Time

Scape Suit

Cost Reduction in Launch/Health/Environment

Propellant Performance (I_{sp})

Fuel + Oxidizer $\rightarrow$ Products + ΔH

$\Delta H = K.E = \frac{1}{2}mv^2$

$I_{sp}= (1/g)\int F(t)dt/\int \dot{M}(t)dt = (1/g)(2\Delta H/m)^{1/2}$

Splash Shield

Search For Hypergolic Fuels

☐ **CEA-Evaluation:** **Identify Better Fuels**

	N_2O_4/MMH	N_2O_4/HEHN	N_2O_4/HEATN
KE(MJ kg^{-1})	4.7	3.9	4.0
ρ(kg m^{-3})	1189	1424	1454
FOM	1.0	1.03	1.05

☐ **Definition: A Pair of Compounds, Upon Contact, Chemically React and Release Sufficient Heat to Spontaneously Ignite**

☐ **Discovery/Research of Hypergolic Propellants: 1930's, Germany (e.g. BMW)**

☐ **No *a Priori* Method to Predict Hypergolicity: NEW Fuel & Oxidizer Hypergol Pair Must be Experimentally Verified!**

Screening Fuels For Hypergolicity

Drop-test Apparatus Employed: O/F = ~ 20

Fuel	IRFNA	N_2O_4	WFNA
CH_3NHNH_2 (L) (MMH)	HGI	HGI	HGI
$HOCH_2CH_2N^+H_2NH_2$ NO_3^- (L) (HEHN)	HGI*	VR	HGI*
(1-ethan-2-ol)-4-amino-1,2,4-triazolium nitrate (L) (HEATN)	SR	VR	
1H-1,2,3-triazole (L)	SR	SR	
1-amino-1,2,3-triazole (M)	HGI*		
3-methyl-1-amino-1,2,3-triazolium nitrate (S)	VR	VR	
▽—≡—H (L)	VR	VR	VR
▽ —≡—▽ (L)	HGI*	HGI*	HGI*
▽ —≡—≡—▽ (L)	HGI*	HGI*	HGI*

HGI=hypergolic ignition, VR=vigorous reaction, SR=slow reaction. At room temperature, fuel is solid (S), liquid (L), or heated to its melting point (M)
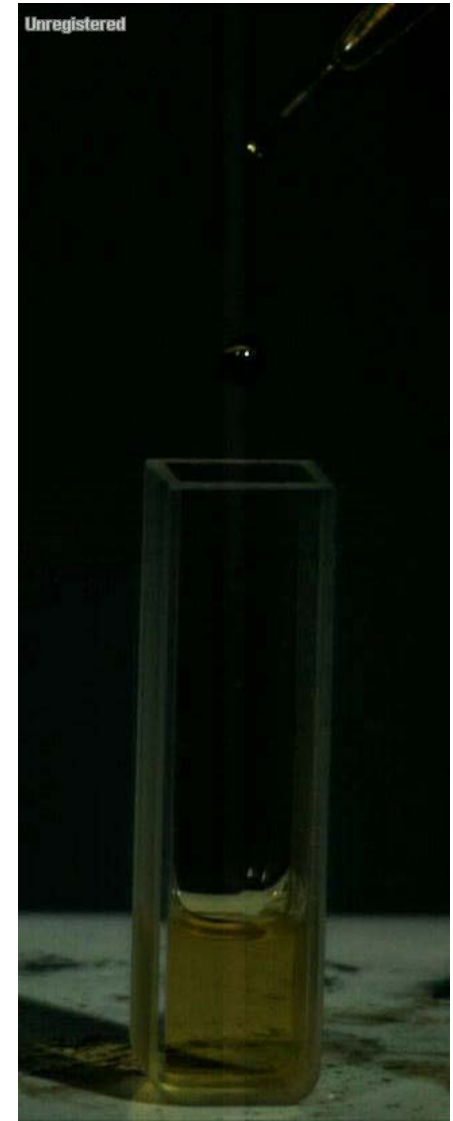*New hypergols

Fuel Functionality Affects Ignition
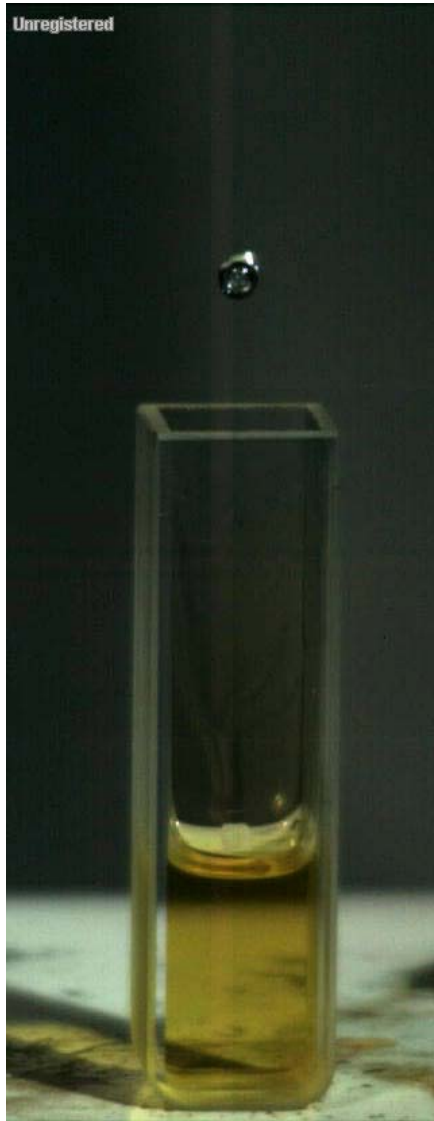
WFNA / $\triangledown$—≡—$\triangledown$ is Hypergolic

$\triangledown$—≡—H

Not Hypergolic

$\triangledown$—≡—≡—$\triangledown$

Is Hypergolic;
ID = 5.0 ms

Complexity of the Pre-ignition Chemistry

$\nabla\!-\!\!\equiv\!\!-\!\nabla$ / N_2O_4

ID = 40.6 ms

New Hypergolic Fuels: Conclusions

- **Characterization of Pre-ignition Chemistry is the Key for Designing new Hypergols**

- **Apply Spectroscopic Probing Tools**
  - **Rapid-Scan FTIR**
  - **Time-Resolved Raman**
  - **Time-Resolved Emission**
  - **High Speed Video**

- **Develop Global Initiatory Mechanism**

- **Construct Pre-Ignition Models**

- **Kinetic Modeling of Ignition**

- **Tune Fuel Chemical Functionalities**

- **Apply Quantum Chemistry Tools**
  - **ΔH of Intermediates**
  - **PES (Reaction Coordinates)**
  - **Reaction Rates**

- **Provide Initial Rationale to Experimental Observations**

Focused/Intelligent Approach to new Synthesis of Hypergolic Fuels

Closing Remarks

- **Acknowledgements:**
  - ❑ **AFOSR**
    - ■ **Drs. M. Berkin & M. Berman (\$\$\$\$)**
  - ❑ **AFRL/PRSP**
    - ■ **Drs. Alfano (Experimental), Mills & Boats (Theory), Suri & Hawkins (Synthesis)**

- **Career in the Government:**
  - ❑ **DoD**
    - ■ **AFRL, ONR, ARL, etc**
  - ❑ **DoE**
    - ■ **LLNL, ANL, ONL, LANL, etc**
  - ❑ **DoC**
    - ■ **NOAA, NIST, etc**
  - ❑ **NASA**
    - ■ **Dryden, Ames, JPL, etc**
  - ❑ **And Many More …….**

- **Web Resources:**
  - ❑ **American Chemical Society** **www.chemistry.org**
  - ❑ **Edwards AFB** **www.edwards.af.mil**
  - ❑ **NASA** **www.nasa.gov**
  - ❑ **New Scientist** **www.sciencesjob.com**

Backup Slides

UV/Vis Plumes

Radiance Data   **Spectral Data**
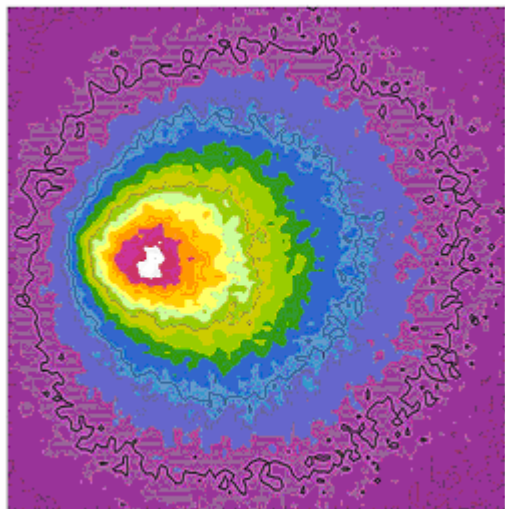
⇔ **Plume Data** ⇔

⇕

Modeling Studies

⇕

Laboratory Studies

⇕

Chemiluminescent Processes

⇕

Identify Spacecraft Atmospheric Interactions

282.2-nm Signal

CHBr$_3$ Photolysis, 2 Torr He

(Plot: 282.2-nm chemiluminescence (counts) vs time (μs))
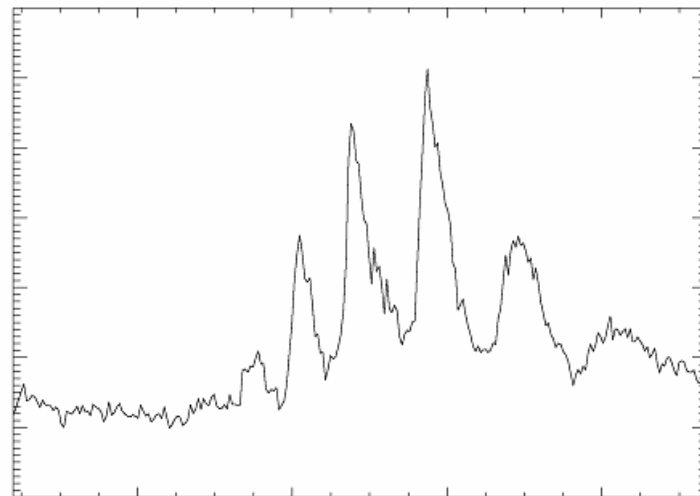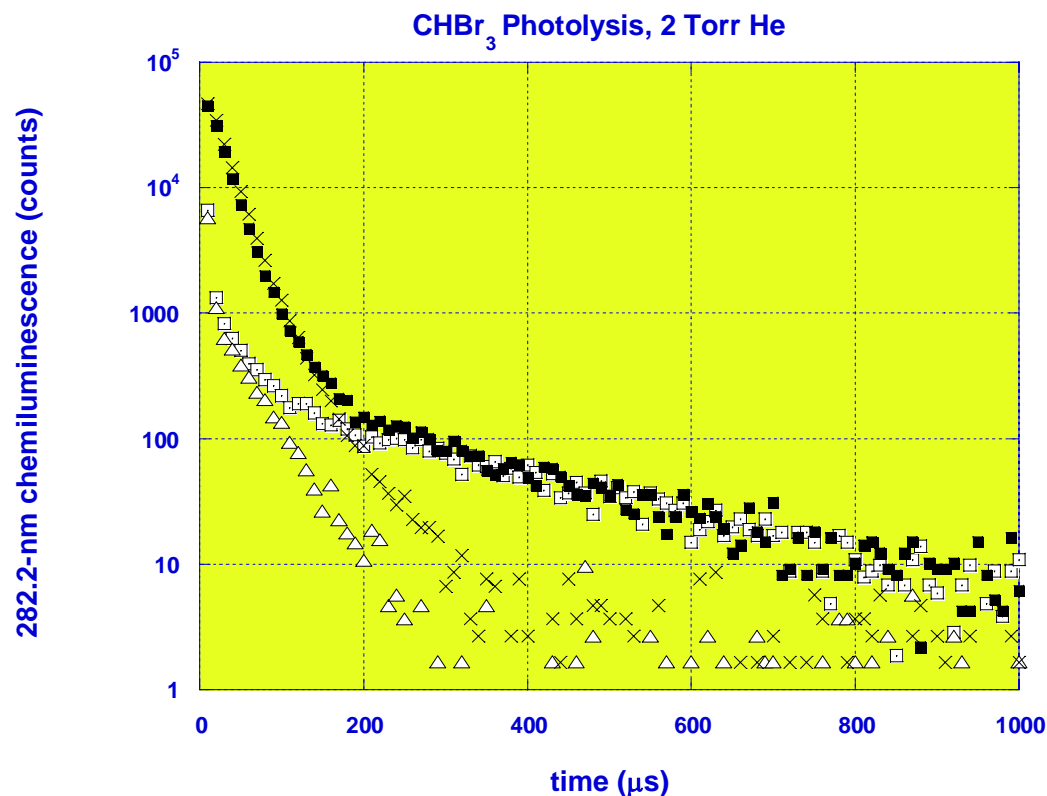
☐ **Absence of O-atoms**

X-trace: (O$_2$, 8.8 x 10^{14})
△-trace: (O$_2$) + (CH$_4$, 5.0 x 10^{15})

↓

CH(X$^2\Pi$) + O$_2$ → CO + OH(A)

CH(a$^4\Sigma^-$) + O$_2$ → CO + OH(A)

☐ **5.0 x 10^{13} of O-atoms**

■-trace: (O$_2$, 8.8 x 10^{14})
☐-trace: (O$_2$) + (CH$_4$, 5.0 x 10^{15})

↓

CBr$_2$ + O → CO + Br$_2$(D)

(CBr$_2$ + CH$_4$) Slow Reaction

Br$_2$*-Chemiluminescence

CHBr$_3$, Excess CH$_4$ & O-atoms, 2 Torr He

☐ **Laser off**

$$CHBr_3 + O \rightarrow CBr_3 + OH$$
$$CBr_3 + O \rightarrow CBr_2 + BrO$$

$\downarrow$

$$CBr_2 + O \rightarrow Br_2^* + CO$$

☐ **Laser on**

$$Br_2^* \propto (Fluence)^1$$

$\downarrow$

$$CHBr_3 + h\nu \rightarrow CHBr_2^* + Br$$
$$CHBr_3 + h\nu \overset{?}{\rightarrow} CBr_2 + HBr$$
$$CHBr_2^* + h\nu \nrightarrow CBr_2 + H$$
$$CHBr_2^* + O \nrightarrow Br_2^* + HCO$$
$$CHBr_2 + O \rightarrow CBr_2 + OH$$
$$CHBr_2^* + O \nrightarrow CBr_2 + OH(A)$$
$$CHBr^* + O \nrightarrow CBr + OH(A)$$
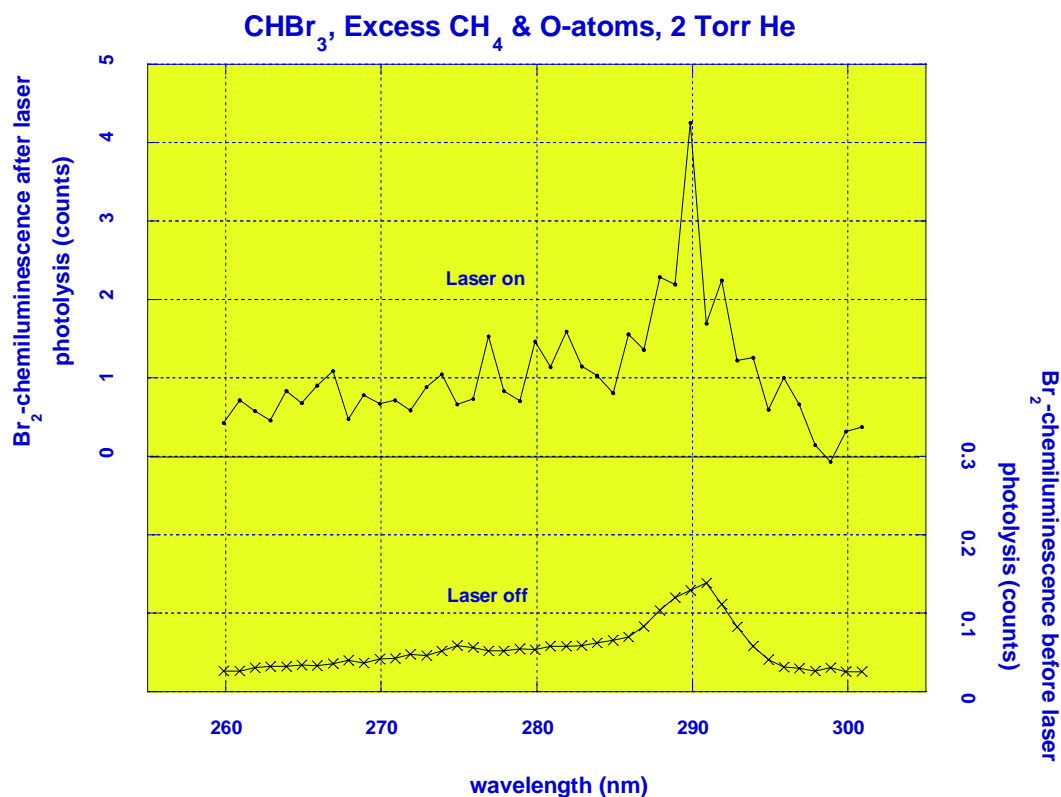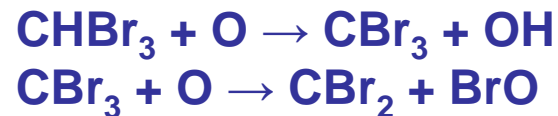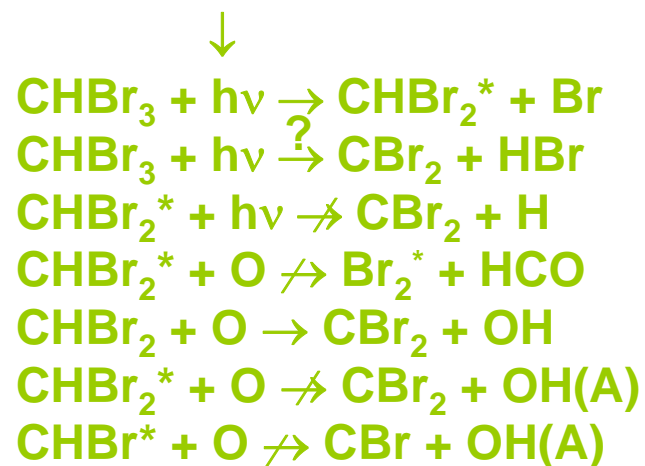
Time Resolved Br$_2$*-Signal

CHBr$_3$ Photolysis, Excess CH$_4$, Excess O-atoms, 2 Torr He

y-axis: 289.9-nm chemiluminescence signal (counts)
x-axis: time (μs)

inset y-axis: ln[int. intensity]
inset x-axis: ln[laser fluence]
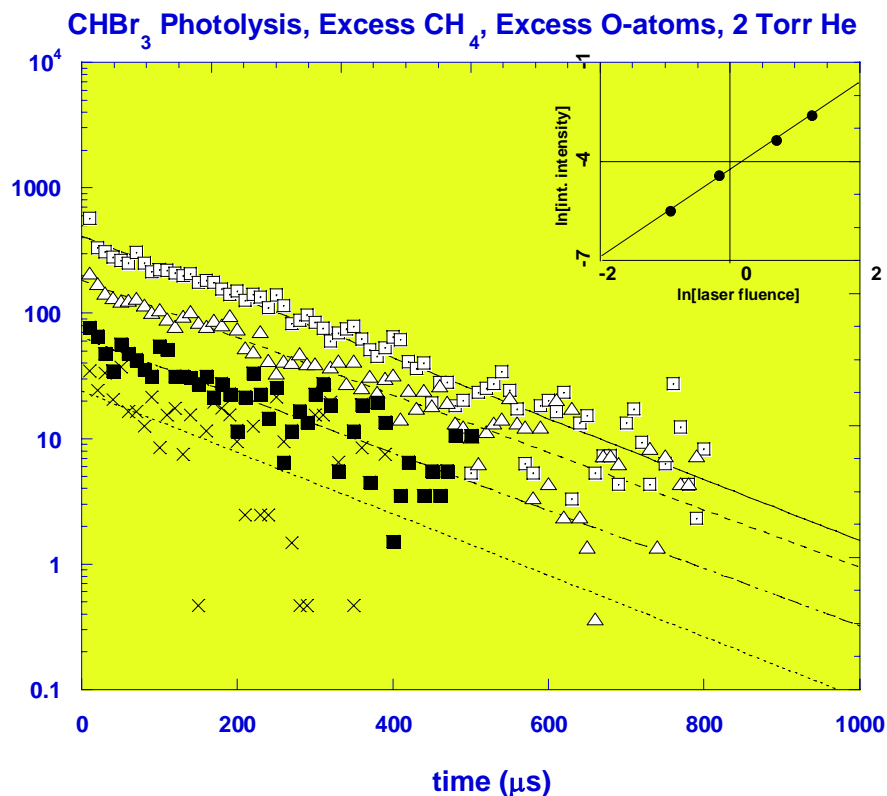
- ❑ **Fast Br$_2$* Rise**
- ❑ **Also:**

$k_{O_2} < 9 \times 10^{-14}$
$k_{CH_4} < 7 \times 10^{-14}$
$k_O = (5.4 \pm 1.0) \times 10^{-11}$

↓

CHBr$_3$ + hν → CBr$_2$ + HBr

Less Important
CBr$_3$ + hν → CBr$_2$ + Br

- ❑ **Since:**

CBr$_4$ + hν → CBr$_3$* + Br
↓ $\{$ ϕ?
CBr$_2$ + Br

CBr$_4$ + hν → CBr$_2$ + Br$_2$ { ϕ?
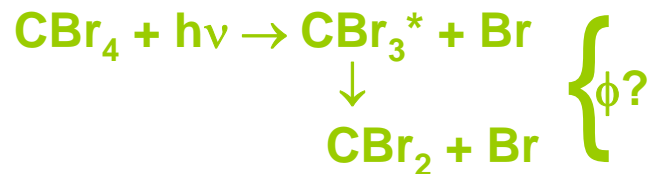
CO* Production Mechanism

$$CH^{\#} + O \rightarrow \{HCO\}^* \rightarrow CO^* + H$$

$$CO^* \xrightarrow{M} CO(X,a,a',d,A)$$
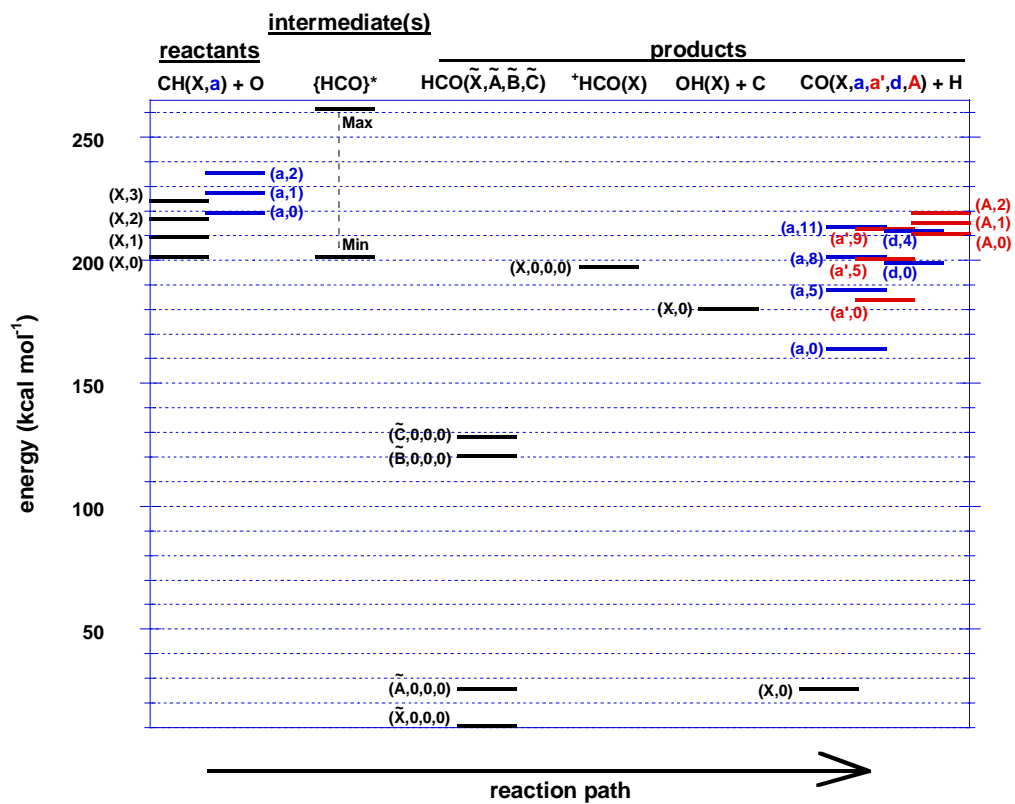
Hypergolic Action

☐ **No *a Priori* Method:** Hypergolicity Between any Pair of Fuel & Oxidant System Must be Experimentally Verified

☐ **Know Your Calories:** < 0.05 cc of a Fuel can Lead to a Spectacular Interaction With an Oxidizer

$$2N_2H_4 + N_2O_4 \rightarrow 3N_2 + 4H_2O \quad \Delta H = -279 \text{ kcal/mol (51 mg = 220 calories)}$$